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APPLICATION FOR LETTERS PATENT

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**Methods of Cleaning Surfaces of Copper-
Containing Materials, and Methods of Forming
Openings to Copper-Containing Substrates**

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1 **Methods of Cleaning Surfaces of Copper-Containing Materials,**
2 **and Methods of Forming Openings to Copper-Containing Substrates**

3 **TECHNICAL FIELD**

4 The invention pertains to methods of cleaning surfaces of copper-
5 containing materials. In particular embodiments, the invention pertains
6 to semiconductor processing methods of forming openings to copper-
7 containing substrates.

8
9 **BACKGROUND OF THE INVENTION**

10 Copper has a relatively high conductance compared to many other
11 elements, and accordingly can be desired for utilization as a wiring layer
12 in various circuitry applications. For instance, in semiconductor
13 processing applications, it can be desired to provide copper wiring layers
14 as electrical paths to various integrated circuit components.

15 A difficulty in utilizing copper in semiconductor processing
16 applications is that it can be difficult to clean. For instance, copper-
17 containing materials will frequently have a surface to which electrical
18 connection with other conductive components is ultimately to occur.
19 Formation of such electrical connection will frequently involve providing
20 a conductive material over the surface of the copper-containing material.
21 The conductive material is intended to physically contact the surface of
22 the copper-containing material to form an electrical connection with the
23 copper-containing material. However, if the surface of the copper-

1 containing material is partially or entirely covered with debris, the
2 physical connection of the conductive material and copper surface can be
3 impaired. Such impairment can lead to attenuation of electrical current
4 passing between the copper-containing layer and the conductive material
5 formed thereover.

6 It would be desirable to develop improved methods of cleaning
7 copper-containing surfaces to remove debris from over the surfaces prior
8 to forming conductive materials thereon.

9 10 SUMMARY OF THE INVENTION

11 In one aspect, the invention encompasses a semiconductor
12 processing method of cleaning a surface of a copper-containing material
13 by exposing the surface to an acidic mixture comprising Cl^- , NO_3^- and
14 F^- .

15 In another aspect, the invention includes a semiconductor
16 processing method of forming an opening to a copper-containing
17 substrate. Initially, a mass is formed over the copper-containing
18 substrate. The mass comprises at least one of a silicon nitride and a
19 silicon oxide. An opening is etched through the mass and to the
20 copper-containing substrate. A surface of the copper-containing substrate
21 defines a base of the opening, and is referred to as a base surface.
22 The base surface of the copper-containing substrate is at least partially
23 covered by at least one of a copper oxide, a silicon oxide or a copper

1 fluoride. The base surface is cleaned with a cleaning solution comprising
2 hydrochloric acid, nitric acid and hydrofluoric acid to remove at least
3 some of the at least one of a copper oxide, a silicon oxide or a copper
4 fluoride from over the base surface.

5 6 **BRIEF DESCRIPTION OF THE DRAWINGS**

7 Preferred embodiments of the invention are described below with
8 reference to the following accompanying drawings.

9 Fig. 1 is a diagrammatic, fragmentary, cross-sectional side view of
10 a semiconductor wafer fragment at a preliminary step of a processing
11 method of the present invention.

12 Fig. 2 is a view of the Fig. 1 wafer fragment shown at a
13 processing step subsequent to that of Fig. 1.

14 Fig. 3 is a view of the Fig. 1 wafer fragment shown at a
15 processing step subsequent to that of Fig. 2.

16 17 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

18 This disclosure of the invention is submitted in furtherance of the
19 constitutional purposes of the U.S. Patent Laws "to promote the progress
20 of science and useful arts" (Article 1, Section 8).

21 The invention encompasses utilization of a mixture comprising Cl^- ,
22 NO_3^- and F^- for cleaning surfaces of copper-containing materials. Such
23 mixture can be formed by, for example, combining an HCl solution

(which can be obtained as, for example, a 36% (by weight) solution of HCl in water), an HF solution (which can be obtained as, for example, a 49% (by weight) solution of HF in water), an HNO₃ solution (which can be obtained as, for example, a 70% (by weight) solution of HNO₃ in water) and H₂O. The acidic mixture can thus be a cleaning solution comprising hydrochloric acid, nitric acid and hydrofluoric acid.

If the cleaning solution is made by mixing water with the above-described 36% hydrochloric acid solution, 49% hydrofluoric acid solution, and 70% nitric acid solution, the relative amounts of the combined water and solutions can be, for example, as follows. The hydrochloric acid solution can be provided to a concentration so that there are from about 2½ parts of water added per 1 part HCl solution to about 10 parts of water added per 1 part of HCl solution. The nitric acid solution can be provided so that there are from about 75 parts of water added per 1 part nitric acid solution to about 300 parts of water added per 1 part nitric acid solution. The hydrofluoric acid solution can be provided so that there are from about 150 parts of water added per 1 part hydrofluoric acid solution to about 600 parts of water added per 1 part of hydrofluoric acid solution. A preferred composition will comprise about 300 parts of water combined with about 60 parts of HCl solution, about 2 parts of nitric acid solution, and about 1 part of hydrofluoric acid solution.

The mixtures formed by the above-described combinations will preferably consist essentially of Cl^- , NO_3^- , and F^- , together with equilibrium components of H_3O^+ and H_2O . The equilibrium components of H_3O^+ and H_2O will be understood by persons of ordinary skill in the art to comprise chemicals in equilibrium with H_3O^+ and H_2O , such as, for example, OH^- (i.e., the hydroxide anion). As is known to persons of ordinary skill in the art, there is some concentration of hydroxide anion present in aqueous solutions, even at acidic pHs. Another way of describing a mixture of the present invention is as an aqueous mixture comprising non-aqueous components consisting essentially of Cl^- , NO_3^- and F^- , or, in particular embodiments, comprising non-aqueous components consisting of Cl^- , NO_3^- and F^- . Such description considers the equilibrium components of H_3O^+ and H_2O to be aqueous components of the mixture. Yet another way of describing a mixture of the present invention is that such mixture is a solution in which the only non-hydroxide anions consist essentially of Cl^- , NO_3^- and F^- , or in particular embodiments, consist of Cl^- , NO_3^- and F^- .

An advantage of using an acidic solution comprising Cl^- , NO_3^- and F^- for cleaning copper in semiconductor fabrication processes is that such solution can remove a variety of common contaminants in a single processing step. For instance, hydrochloric acid can remove copper oxides (such as, for example, Cu_2O and CuO), hydrofluoric acid can remove silicon oxides (for example, SiO_2), as well as copper oxides; and

1 nitric acid can remove elemental copper. The acidic solution of the
2 present invention can also remove copper fluorides (CuF and CuF_2).

3 A semiconductor processing method incorporating a copper cleaning
4 procedure encompassed by the present invention is described with
5 reference to Figs. 1-3.

6 Referring first to Fig. 1, a semiconductive material wafer
7 fragment 10 is illustrated at a preliminary processing step. Wafer
8 fragment 10 comprises a semiconductive material substrate 12 having a
9 copper-containing material 14 formed thereover. Substrate 12 can
10 comprise, for example, a monocrystalline silicon wafer having various
11 levels of circuitry formed thereover. To aid in interpretation of the
12 claims that follow, the terms "semiconductive substrate" and
13 "semiconductor substrate" are defined to mean any construction
14 comprising semiconductive material, including, but not limited to, bulk
15 semiconductive materials such as a semiconductive wafer (either alone or
16 in assemblies comprising other materials thereon), and semiconductive
17 material layers (either alone or in assemblies comprising other materials).
18 The term "substrate" refers to any supporting structure, including, but
19 not limited to, the semiconductive substrates described above.

20 Copper-containing material 14 can comprise, for example, a copper
21 alloy, a copper compound, or elemental copper, and can be formed by,
22 for example, sputter deposition. In particular embodiments, copper-
23 containing material 14 will consist essentially of elemental copper (or

1 consist of elemental copper) and defines a wiring layer for connecting
2 various circuitry components (not shown) associated with fragment 10.

3 A mass 16 is formed over copper-containing material 14. Mass 16
4 can comprise, for example, one or more insulative materials. In
5 particular embodiments, mass 16 comprises at least one of a silicon
6 nitride (for example, Si_3N_4) and a silicon oxide (for example, SiO_2 or a
7 doped oxide, such as, for example, borophosphosilicate glass). The
8 shown mass 16 comprises two layers 18 and 20 which are formed one
9 atop the other. One of layers 18 and 20 can comprise a silicon oxide,
10 and the other of the layers can comprise a silicon nitride. For instance,
11 layer 18 could consist essentially of Si_3N_4 (or in particular embodiments
12 consist of Si_3N_4) and layer 20 could consist essentially of SiO_2 (or in
13 particular embodiments consist of SiO_2). Such layers 18 and 20 can be
14 formed by, for example, chemical vapor deposition.

15 Referring to Fig. 2, an opening 22 is etched through mass 16, and
16 specifically is etched through both of layers 18 and 20. Opening 22 can
17 be formed by, for example, photolithographic processing wherein a
18 photoresist masking layer (not shown) is formed over mass 16 and
19 patterned to protect some of mass 16 while leaving a portion of mass 16
20 exposed to etching conditions which ultimately form opening 22.

21 Opening 22 extends to an upper surface 15 of copper-containing
22 material 14. Surface 15 defines a base of opening 22, and the portion
23 of surface 15 within opening 22 can be referred to as a base surface.

1 Base surface 15 is partially covered by contaminating particles 24.
2 Such contaminating particles can comprise, for example, one or more of
3 a copper oxide, a silicon oxide, or a copper fluoride. Additionally,
4 particles 24 can comprise elemental copper leftover from a sputter
5 deposition of copper-containing material 14. The copper oxide, silicon
6 oxide or copper fluoride particles can be formed, for example, during the
7 etch through layers 18 and 20. For instance, the silicon oxide can be
8 formed by either oxidation of a silicon nitride component of mass 16,
9 or by debris occurring during the etch of a silicon oxide component of
10 mass 16. As another example, copper oxide can be formed from
11 portions of copper-containing material 14 exposed to etching conditions,
12 if such conditions comprise oxidative components. As yet another
13 example, copper fluoride can be formed from portions of copper-
14 containing material 14 exposed to etching conditions if such conditions
15 comprise a fluorine-containing etchant such as, for example, CF_4 .

16 Although base surface 15 is shown to be only partially covered by
17 contaminating particles 24, it is to be understood that such particles can
18 entirely cover base surface 15. The particles 24 can also be deposited
19 on the sidewalls of opening 22 and on the surface of 20.

20 Although the contaminating particles 24 are described as being
21 formed during formation of opening 22, it is to be understood that
22 particles 24 could be formed during other processing steps, such as, for
23

1 example, as residuals from a chemical-mechanical polishing processing
2 step.

3 Referring to Fig. 3, contaminating particles 24 (Fig. 2) are
4 removed from base surface 15 by cleaning such surface with an acidic
5 mixture comprising Cl^- , NO_3^- and F^- . More specifically, base surface 15
6 is cleaned by exposing the surface to the mixture of the present
7 invention which is described above for removing copper oxide, silicon
8 oxide, copper fluoride, and elemental copper from over base surface 15
9 in one cleaning step. Such cleaning solution preferably is an aqueous
10 mixture comprising non-aqueous components, with the non-aqueous
11 components consisting essentially of Cl^- , NO_3^- and F^- . The cleaning
12 mixture can have such preferred composition at least until base
13 surface 15 is exposed to the mixture. Once base surface 15 is exposed
14 to the mixture, a composition of the mixture can change to include
15 components released from particles 24 (Fig. 2) during the removal of
16 particles 24 from over base surface 15 with the mixture.

17 The exposure of base surface 15 to an acidic mixture comprising
18 Cl^- , NO_3^- and F^- can occur for a time of from about 30 seconds to
19 about one hour at a temperature of from about 10°C to about 40°C ,
20 and at atmospheric pressure. The temperature can comprise, for
21 example, room temperature (typically from 20°C to 26°C).

22 Relative amounts of F^- , Cl^- and NO_3^- within an acidic cleaning
23 mixture of the present invention can be varied depending upon particular

1 cleaning conditions. For instance, if a large amount of silicon oxide
2 contamination is expected to be present, the concentration of F^- can be
3 increased relative to the concentrations of Cl^- and NO_3^- . On the other
4 hand, if elemental copper is particularly problematic, the concentration
5 of NO_3^- can be increased relative to the concentrations of Cl^- and F^- .
6 Further, if copper oxides are particularly problematic, the concentration
7 of Cl^- can be increased relative to the concentrations of NO_3^- and F^- .
8 Also, it can be desirable to increase the total concentrations of Cl^- , NO_3^-
9 and F^- to accomplish faster cleaning of a copper-containing substrate.
10 Faster cleaning can also be accomplished by increasing a temperature of
11 the cleaning solution and/or a temperature of the copper-containing
12 material during a cleaning process.

13 Relative concentrations of Cl^- , NO_3^- and F^- can also be varied to
14 avoid having one or more of the various anions etching non-
15 contaminating portions of wafer fragment 10. For instance, a method
16 of exposing base surface 15 to a cleaning solution of the present
17 invention is to dip a wafer comprising fragment 10 into a cleaning
18 solution of the present invention for a time of about 5 minutes. Such
19 dip would expose layers 18 and 20 to the cleaning solution, as well as
20 exposing base surface 15 to the cleaning solution. If one or both of
21 layers 18 and 20 comprise silicon dioxide, the silicon dioxide would be
22 expected to be etched by F^- present in the cleaning solution. Such
23 etching could alter a configuration of layers 18 and 20 if the

1 concentration of F^- were sufficiently high, or if the time of exposure
2 were sufficiently long. For instance, if an interface 19 is defined at a
3 location where layers 18 and 20 join, and if it is considered that one of
4 layers 18 and 20 is silicon nitride and the other is silicon dioxide, then
5 the exposure to F^- in the cleaning solution may form divots at
6 locations 21 where interface 19 is exposed along sidewalls of opening 22.
7 A method of avoiding such divot formation is to adjust a concentration
8 of F^- within the cleaning solution so that the F^- concentration is only
9 enough to remove contaminating particles 24 from base surface 15. In
10 other words, to adjust the concentration of F^- within the cleaning
11 solution so that there is enough F^- to remove particles 24, but not
12 enough to detrimentally affect exposed silicon oxide surfaces of mass 16
13 during the time of an etch.

14 Preferably, if a silicon oxide containing surface of mass 16 is
15 exposed to an acidic cleaning solution of the present invention during a
16 cleaning of base surface 15, the concentration of F^- within the acidic
17 mixture will be such that less than 5 Angstroms of silicon oxide is
18 removed from the exposed surface of mass 16 during the cleaning of the
19 base surface.

20 In compliance with the statute, the invention has been described
21 in language more or less specific as to structural and methodical
22 features. It is to be understood, however, that the invention is not
23 limited to the specific features shown and described, since the means

1 herein disclosed comprise preferred forms of putting the invention into
2 effect. The invention is, therefore, claimed in any of its forms or
3 modifications within the proper scope of the appended claims
4 appropriately interpreted in accordance with the doctrine of equivalents.
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